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SUMMARY

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A set of equations is developed from which the chemical composition and real-gas correction terms for the thermodynamic properties of a reacting gas mixture at relatively high pressure can be calculated. This method utilizes the second virial coefficients of each of the species in their pure state and employs the Lewis and Randall rule to obtain the properties of the mixture. Results based on the present approximate calculation are compared with calculations of Hilsenrath and Klein for air. It is found that the present approximate method yields essentially the same chemical composition for the mixture as was obtained by the more rigorous method at a temperature of 6,000° K and pressures of about 2,500 atm and 4,500 atm. The corresponding real-gas correction terms for the enthalpy and entropy of the mixture are also in very good agreement with the results presented by Hilsenrath and Klein. Some considerations regarding application of this simplified method to reacting gas mixtures other than high-temperature air are also presented.

INTRODUCTION

The equilibrium composition and thermodynamic properties of reacting gas mixtures are required for the solution of a large number of practical problems. In most problems the gas system may be regarded as a reacting mixture of perfect gases, provided the gas density is not too great. As higher gas densities are considered, the assumption of a mixture of perfect gases becomes less valid because of the increasing importance of intermolecular forces between the molecules and atoms in the mixture.

One practical problem involves the calculation of the thermodynamic properties and flow parameters in hypersonic test facilities in which the stagnation temperature and pressure are quite high. In this application, the departure due to intermolecular force effects can be significant and their influence should be taken into account. The problem exists for test facilities that simulate the composition of planetary atmospheres as well as for those that use air.

General methods for calculating the real-gas composition and thermodynamic properties of reacting gas mixtures based on a virial equation of state may be found in references 1, 2, and 3. The calculation procedures required to apply these general methods are difficult in that the equilibrium constants based on partial pressures for the reactions and the real-gas effects for each species in the mixture are coupled to the chemical composition. The general solution thus requires an involved iteration technique.

The purpose of this report is to develop the equations for and to test the validity of a simple approach to the calculation of the chemical composition and thermodynamic properties of reacting gas mixtures under relatively high pressures. The present approach considers only the second virial corrections. The Lewis and Randall rule (discussed at length in ref. 1) is applied to obtain the composition and thermodynamic properties of the reacting gas mixture from the properties of the various species in their pure states. As an approximate method for taking real-gas effects into account for gas mixtures, the Lewis and Randall rule is often used. This rule states that the fugacity of a given species in a mixture is equal to the mole fraction of that species multiplied by the fugacity of the species in its pure state at the temperature and total pressure of the mixture.

The expressions for correction terms to be applied to the mixture properties for a reacting mixture of perfect gases are derived. After the appropriate equations have been developed and the method of calculation has been presented, a discussion concerning the applicability of the Lewis and Randall rule is given. A sample calculation is then made for air and the results are compared with the results presented by Hilsenrath and Klein in reference 4.

SYMBOLS

$a_{i,k}$	number of atoms of kth element in a molecule of ith species
$b_{k,k+1}$	atom ratio of kth element to (k + 1)th element in gas mixture, either as element or in chemical combination
B	second virial coefficient based on molar specific volume
$c_{p,i}$	heat capacity at constant pressure of ith species
$c^{o}_{p,i}$	heat capacity at constant pressure of ith species based on a perfect gas
f_i	fugacity of ith species in mixture
$f_{i,p}$	fugacity of pure ith species at temperature and total pressure of mixture
ΔF^{o}	standard-state free energy change for a reaction

H	enthalpy per mole
H^o	enthalpy per mole based on perfect gas
$\overline{H}$	enthalpy per mole of mixture
$\overline{H}^o$	enthalpy per mole of mixture based on perfect gas relations; when $\overline{H}^o$ appears in an expression subscripted with x_i, the mixture is the real-gas composition
$\Delta H_{f,i}$	standard enthalpy of formation of ith species
K_f	equilibrium constant based on fugacities
K_p	equilibrium constant based on partial pressures
K_x	equilibrium constant based on mole fractions
K_γ	equilibrium constant correction, defined by equation (17)
M_i	molecular weight of ith species
$\overline{M}$	molecular weight of gas mixture
$\overline{M}_{ref}$	molecular weight of gas mixture at an arbitrary reference state
p	pressure
p_i	partial pressure of species i
R	universal gas constant
S	entropy per mole
S^o	entropy per mole based on perfect gas
$\overline{S}$	entropy per mole of mixture
$\overline{S}^o$	entropy per mole of mixture based on perfect gas relations; when $\overline{S}^o$ appears in an expression subscripted with x_i, the mixture is the real-gas composition
$\Delta S_{f,i}$	standard entropy of formation of ith species
T	temperature
v	specific volume per mole
v_i	specific volume per mole of ith species at temperature and total pressure of mixture

$\bar{v}$ specific volume of mixture per mole

$\hat{v}$ specific volume of mixture per unit mass

x_i mole fraction of ith species

$x_{i'}$ mole fraction of i'th species

x_i^o mole fraction of ith species based on perfect gas

Z_i compressibility factor for ith species in pure state at temperature and total pressure of mixture

Z' total compressibility factor of mixture, $\bar{Z}\tilde{Z}$

$\bar{Z}$ compressibility factor of mixture due to real-gas effects

$\tilde{Z}$ molecular weight ratio of mixture, $\frac{\bar{M}_{ref}}{\bar{M}}$

γ_i ratio of fugacity of ith species to pressure in pure state at temperature and total pressure of the mixture

$\nu_{i,j}$ stoichiometric coefficient of ith species in jth reaction

$\Delta\nu$ net difference in stoichiometric coefficients for a reaction

Subscripts:

i ith species

i' i'th species

ii' pair interaction between ith and i'th species

j jth reaction

k kth chemical element in system

T,p,x_i quantity evaluated at T and p of mixture and real-gas composition x_i

$T,\bar{v},x_i$ quantity evaluated at T and $\bar{v}$ of mixture and real-gas composition x_i

DEVELOPMENT OF EQUATIONS

Equilibrium Composition

The procedure for calculating the real-gas[1] equilibrium composition of a system of reacting gases is similar to that used for calculating the composition of a reacting system of perfect gases. The essential difference between the two calculations is in the evaluation of the equilibrium constants in terms of the species mole fractions K_x for the perfect gas and real gas.

Perfect gas.- From arguments given in reference 1, it can be shown that the equilibrium constant in terms of the partial pressures of each species K_p is related to the standard-state free energy change for a reaction ΔF^o by the expression

$$-\Delta F^o = RT \log_e K_p \tag{1}$$

if it is assumed that the reacting species are perfect gases. The standard-state free energy change for a given reaction ΔF^o is a function of temperature only. The equilibrium constant in terms of partial pressures K_p for a reaction such as

$$aA + bB \rightleftarrows cC + dD$$

is

$$K_p = \frac{p_C{}^c p_D{}^d}{p_A{}^a p_B{}^b} \tag{2}$$

For a system of perfect gases, the partial pressure of the ith species is related to the mole fraction x_i of that species and total system pressure p by the expression

$$p_i = x_i p \tag{3}$$

If an equilibrium constant for the reaction is defined in terms of the mole fractions

$$K_x = \frac{x_C{}^c x_D{}^d}{x_A{}^a x_B{}^b} \tag{4}$$

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[1]The term "real gas" used herein refers strictly to the effects due to intermolecular forces between molecules or atoms.

it follows then that

$$K_x = K_p p^{-\Delta\nu} \tag{5}$$

where $\Delta\nu = c + d - a - b$. The expression K_x based on the assumption of a reacting system of perfect gases is, from equations (1) and (5),

$$K_x = p^{-\Delta\nu}\exp(-\Delta F^\circ/RT) \tag{6}$$

If there are J independent and simultaneous reactions in a given system, there will be J equations similar to equation (6) - that is,

$$K_{x,j} = p^{-\Delta\nu_j}\exp\left(-\Delta F_j^\circ/RT\right) \qquad (j = 1, 2, \ldots, J) \tag{7}$$

In addition to these J equilibrium expressions, the principle of conservation of mass for the kth chemical element in the reacting system leads to K additional equations. If the quantity $b_{k,k+1}$ is defined as the atom ratio of the kth element to the $(k + 1)$th element in the system, regardless of the chemical species in which the element appears, it is possible to write the following $K - 1$ equations:

$$\frac{\sum_i a_{i,k}x_i}{\sum_i a_{i,k+1}x_i} = b_{k,k+1} \qquad (k = 1, 2, \ldots, K - 1) \tag{8}*$$

where $a_{i,k}$ represents the number of atoms of the kth element in a molecule of the ith chemical species and $a_{i,k+1}$ is the corresponding quantity for the $(k + 1)$th element. (An asterisk following an equation number indicates that the equation is used in the final computations.) An equation which states that the summation of the mole fractions of all species is unity can also be written as

$$\sum_i x_i = 1 \tag{9}*$$

Equations (7) to (9) represent $J + K$ relations which can be solved simultaneously to find the equilibrium chemical composition for a given temperature, pressure, and initial elemental balance based on the assumption of a reacting system of perfect gases.

Real gas.- The real-gas expression corresponding to equation (1), as shown in reference 1, is

$$-\Delta F^{o} = RT \log_e K_f \tag{10}$$

where K_f is the equilibrium constant expressed in terms of the fugacities of the species in the system. The expression for K_f for the aforementioned reaction is

$$K_f = \frac{f_C^{c} f_D^{d}}{f_A^{a} f_B^{b}} \tag{11}$$

where the fugacity at a given temperature is defined in terms of pressure, volume, and temperature by the isothermal equation

$$v_i \, dp = RT \, d \log_e f_{i,p} \tag{12}$$

An additional statement concerning fugacity must also be written to show the relationship between $f_{i,p}$ and p at low pressures - that is,

$$\lim_{p \to 0} \left(\frac{f_{i,p}}{p} \right) = 1 \tag{13}$$

For the real-gas case presented herein, equation (3) is replaced by the Lewis and Randall rule which states that the fugacity of the ith species in a gas mixture in equilibrium f_i equals the mole fraction of that species x_i multiplied by the fugacity of that species in its pure state at the temperature and total pressure of the mixture $f_{i,p}$:

$$f_i = x_i f_{i,p} \tag{14}$$

From this rule, the composition and the thermodynamic properties of a mixture can be calculated in terms of the temperature and total pressure of the system.

A relationship between the equilibrium constant in terms of the fugacities K_f and the mole fractions K_x for the real-gas case can be determined through equation (14). For convenience, the ratio of $f_{i,p}$ divided by the pressure of the system is defined as

$$\gamma_i = \frac{f_{i,p}}{p} \tag{15}$$

It follows that

$$K_f = K_x K_\gamma p^{\Delta\nu} \tag{16}$$

where

$$K_\gamma = \frac{\gamma_C{}^c \gamma_D{}^d}{\gamma_A{}^a \gamma_B{}^b} \tag{17}$$

Equation (16) can be combined with equation (10) for the real-gas case to yield

$$K_x = \frac{1}{K_\gamma} p^{-\Delta\nu} \exp(-\Delta F^\circ/RT) \tag{18}$$

or for each of the J reactions

$$K_{x,j} = \frac{1}{K_{\gamma,j}} p^{-\Delta\nu_j} \exp\left(-\Delta F_j^\circ/RT\right) \qquad (j = 1, 2, 3, \ldots, J) \tag{19}*$$

This real-gas expression for $K_{x,j}$ and the perfect-gas expression given by equation (7) differ by the factor $\frac{1}{K_{\gamma,j}}$. Because all values of γ_i approach unity as the pressure is made small as a result of equation (13), the real-gas expression for $K_{x,j}$ reduces to the perfect-gas expression at low pressures. The quantity $K_{\gamma,j}$ depends only on the properties of the various reacting species in their pure states; a method for calculating $K_{\gamma,j}$ is described in the next section. The expressions for the conservation of mass of each chemical element in the reacting system - that is, equations (8) and (9) - are exactly the same for the real-gas and perfect-gas cases. The equilibrium composition for the real-gas case can, therefore, be determined by simultaneous solution of equations (8), (9), and (19).

Calculation of K_γ.- An expression for calculating the fugacity of a pure gas at a given temperature and pressure is required. The real-gas equation of state for the ith species may be written as

$$pv_i = Z_i RT \tag{20}$$

In the present work it is assumed that the second virial coefficient B_i is sufficient to account for the real-gas behavior so that

$$Z_i = 1 + \frac{B_i}{v_i} \tag{21}$$

where B_i is a function only of temperature for a particular gas. Values of B_i are presented for a number of simple gases in reference 5.

When equation (12) is divided by equation (20) it is found that

$$Z_i \frac{dp}{p} = d \log_e f_{i,p} \tag{22}$$

or

$$(Z_i - 1)\frac{dp}{p} = d \log_e\left(\frac{f_{i,p}}{p}\right) \tag{23}$$

Equations (20) and (21) can be combined to eliminate v_i and then differentiated at constant temperature to obtain

$$\frac{dp}{p} = \frac{2Z_i - 1}{Z_i(Z_i - 1)} dZ_i \tag{24}$$

so that equation (23) can be reduced to

$$d \log_e\left(\frac{f_{i,p}}{p}\right) = \frac{2Z_i - 1}{Z_i} dZ_i \tag{25}$$

This expression is integrated at constant temperature from $\frac{f_{i,p}}{p} = 1$ (and $Z_i = 1$, where $p \to 0$) up to an upper state of $\frac{f_{i,p}}{p}$ and Z_i, so that

$$\gamma_i = \frac{f_{i,p}}{p} = \frac{\exp\left[2(Z_i - 1)\right]}{Z_i} \tag{26}*$$

An explicit expression for Z_i obtained from equations (20) and (21) is

$$Z_i = \frac{1 + \sqrt{1 + \frac{4B_i}{RT} p}}{2} \tag{27}*$$

where only the larger root has been retained because of the requirement that

$$\lim_{B_i \to 0} Z_i = 1$$

It should be mentioned that the quantity Z_i is not the compressibility factor for the ith species in the mixture but a quantity Z_i that is calculated for the pure species at the temperature and total pressure of the mixture as required by the Lewis and Randall rule.

Equation (26) can be used to calculate γ_i for each species in the reacting system at the temperature and total pressure of the system. The quantity $K_{\gamma,j}$ for the jth reaction can then be obtained from the expression

$$K_{\gamma,j} = \prod_{i,\text{products}} \gamma_i^{\nu_{i,j}} \prod_{i,\text{reactants}} \gamma_i^{-\nu_{i,j}} \qquad (28)^*$$

where $\nu_{i,j}$ represents the stoichiometric coefficient for the ith species in the jth reaction.

Real-Gas Corrections for a Pure Gas

The compressibility factor and the real-gas correction terms for the enthalpy and entropy of a reacting mixture of real gases can be determined from the individual real-gas correction terms of the pure gases that make up the mixture. This assumes that the composition is first calculated by the present method. In this section the real-gas correction terms for the enthalpy and entropy are developed for a pure gas. It should be noted that equation (27) may be used directly to obtain Z_i for a given species in the pure state.

Enthalpy correction term.- The enthalpy correction term is the difference between the enthalpy calculated for a pure gas based on a real-gas model and that based on the assumption of a perfect gas at a given temperature and pressure. It can be shown (see, for example, ref. 1) that this difference at temperature T and pressure p is

$$\left(H_i - H_i^o\right)_{T,p} = \int_{p\to 0}^{p} \left[v_i - T\left(\frac{\partial v_i}{\partial T}\right)_p\right] dp \qquad (29)$$

Equation (27) is used to eliminate Z_i from equation (20) in order to obtain an expression for v_i that is a function of p at a fixed value of T. An equation for $\left(\frac{\partial v_i}{\partial T}\right)_p$ can then be obtained by differentiating the expression for v_i. Equation (29) can be integrated at a given value of T to give

$$\left(\frac{H_i - H_i^o}{RT}\right)_{T,p} = (Z_i - 1)\left(1 - \frac{T}{B_i}\frac{dB_i}{dT}\right) \qquad (30)^*$$

where equation (27) has been used to simplify the integrated equation. Reference 5 gives values of $\frac{dB_i}{dT}$ for a number of simple gases for a range of temperature.

Entropy correction term.- The entropy correction term or the difference between the entropy calculated for a pure gas based on a real-gas model and that based on the assumption of a perfect gas at a given temperature and pressure can be written as

$$\left(S_i - S_i^o\right)_{T,p} = \int_{p \to 0}^{p} \left[\frac{R}{p} - \left(\frac{\partial v_i}{\partial T}\right)_p\right] dp \tag{31}$$

where S_i^o and S_i include the entropy of formation for the ith species $\Delta S_{f,i}$. The same equation for $\left(\frac{\partial v_i}{\partial T}\right)_p$ that was used in integrating equation (29) can be used in integrating equation (31). This procedure yields

$$\left(\frac{S_i - S_i^o}{R}\right)_{T,p} = -(Z_i - 1)\left(1 + \frac{T}{B_i}\frac{dB_i}{dT}\right) + \log_e Z_i \tag{32}*$$

where equation (27) has been used to simplify the integrated equation.

Real-Gas Corrections for a Reacting Gas Mixture

The real-gas correction terms for the enthalpy and entropy, as well as the compressibility factor, are developed in this section for a mixture of reacting gases. Because only interactions between like species are considered ir this work, the mixture properties can be calculated from weighted summations of the properties of the pure species that compose the mixture.

Compressibility factor.- It can be shown (for example, in ref. 1) that Amagat's law (as opposed to Dalton's law) for the mixture is required by the Lewis and Randall rule. Thus the mixture equation of state must be based on Amagat's law

$$\bar{v} = \sum_i x_i v_i \tag{33}$$

where $\bar{v}$ denotes the total molar volume of the gas mixture and v_i denotes the molar volume of species i in the pure state at the temperature and total pressure of the gas mixture. The application of the real-gas equation of state

(eq. (20)) for each of the ith species to the expression for fixed values of T and p yields

$$\frac{p\bar{v}}{RT} = \sum_i x_i Z_i \equiv \bar{Z} \qquad (34)^*$$

where $\bar{Z}$ is the real-gas compressibility factor of the reacting mixture. The quantity $\bar{Z}$ for the mixture can, therefore, be calculated directly once the composition and values of Z_i for each species are determined.

It is sometimes desired to express the equation of state for the mixture in terms of specific volume per unit mass $\hat{v}$ rather than specific volume per unit mole $\bar{v}$. These two quantities are related through the molecular weight of the mixture by the equation

$$\hat{v} = \frac{\bar{v}}{\bar{M}} \qquad (35)$$

where

$$\bar{M} = \sum_i x_i M_i \qquad (36)$$

An alternate form of the equation of state of the mixture in terms of $\hat{v}$ is, therefore,

$$\frac{p\hat{v}}{RT} = \frac{\bar{Z}}{\bar{M}} \qquad (37)$$

In systems where chemical reactions occur a reference mixture is sometimes assumed for which the molecular weight is $\bar{M}_{ref}$. It is then possible to define a ratio of $\bar{M}_{ref}$ to the molecular weight of the mixture for values of T and p as

$$\tilde{Z} = \frac{\bar{M}_{ref}}{\bar{M}} \qquad (38)$$

From equations (37) and (38) it follows that

$$\frac{p\hat{v}}{\left(\frac{R}{\bar{M}_{ref}}\right)_T} = \tilde{Z}\bar{Z} \equiv Z' \qquad (39)^*$$

The quantity Z' is the total compressibility factor of the mixture, and the quantity $\frac{R}{\overline{M}_{ref}}$ is a gas constant for the mixture per unit mass of the mixture.

Enthalpy correction term.- The enthalpy of a mixture, in which only pair interactions between like species are considered, is the weighted summation of the enthalpy of each species in its pure state. The enthalpy correction term or difference between the enthalpy of the mixture calculated for a real-gas model $\overline{H}$ and that calculated for a mixture of perfect gases $\overline{H}^o$ at the same temperature and pressure is, therefore,

$$\left(\overline{H} - \overline{H}^o\right)_{T,p} = \sum_i x_i H_i - \sum_i x_i^o H_i^o \qquad (40)$$

where

$$H_i = \int c_{p,i}\, dT + \Delta H_{f,i}$$

$$H_i^o = \int c_{p,i}^o\, dT + \Delta H_{f,i}$$

and the lower limit of integration is taken to be the temperature at which $\Delta H_{f,i}$ is evaluated. By adding and subtracting $\sum_i x_i H_i^o$ from the right-hand side of equation (40) and then dividing the result by RT, the nondimensional real-gas enthalpy correction for the mixture can be written as

$$\left(\frac{\overline{H} - \overline{H}^o}{RT}\right)_{T,p} = \sum_i x_i \left(\frac{H_i - H_i^o}{RT}\right)_{T,p} + \sum_i \left(x_i - x_i^o\right)\frac{H_i^o}{RT} \qquad (41)^*$$

This correction term should be added to the nondimensional enthalpy of a mixture at values of T and p based on a perfect-gas calculation $\overline{H}^o/RT$ in order to obtain the real-gas value of the nondimensional enthalpy of the mixture $\overline{H}/RT$ for the same set of values of T and p.

The quantities x_i and x_i^o are found by the method presented in the section entitled "Equilibrium Composition." The correction term $\left(\frac{H_i - H_i^o}{RT}\right)_{T,p}$ for

each species is calculated from equation (30). The quantity H_i^o of the pure species based on a perfect gas calculation can be obtained from reference 6 for a number of species.

Entropy correction term.- The correction term for the nondimensional entropy of a mixture of reacting gases has terms similar to those in equation (41) for the nondimensional enthalpy, as well as an additional term to account for the difference in the mole fractions of each species calculated for the real-gas and perfect-gas cases. The entropy correction term is therefore

$$\left(\frac{\bar{S} - \bar{S}^o}{R}\right)_{T,p} = \sum_i x_i \left(\frac{S_i - S_i^o}{R}\right)_{T,p} + \sum_i \left(x_i - x_i^o\right)\left(\frac{S_i^o}{R}\right)_{T,p}$$

$$- \sum_i \left(x_i \log_e x_i - x_i^o \log_e x_i^o\right) \qquad (42)^*$$

The quantity $\left(\frac{S_i - S_i^o}{R}\right)_{T,p}$ for each species can be obtained from equation (32). This correction term should be added to the nondimensional entropy of a mixture at values of T and p based on a perfect-gas calculation $\bar{S}^o/R$ in order to obtain the real-gas value of the nondimensional entropy of the mixture $\bar{S}/R$ for the same set of values of T and p. The entropy of the pure species based on perfect-gas calculation can be obtained from tabulated quantities presented in the literature, such as those found in reference 6.

Alternative correction terms.- In the foregoing method for calculating the real-gas thermodynamic properties of a reacting mixture, the perfect-gas equilibrium composition x_i^o must be determined. An alternative method can be developed in which it is not necessary to calculate the perfect-gas composition x_i^o. The procedure is to construct pseudo-perfect-gas-mixture thermodynamic properties which are based on the real-gas composition x_i, rather than on the perfect-gas composition x_i^o as was done to arrive at the correction factors given by equations (41) and (42).

The nondimensional pseudo-perfect-gas enthalpy of the mixture is

$$\left(\frac{\bar{H}^o}{RT}\right)_{T,p,x_i} = \sum_i x_i \frac{H_i^o}{RT} \qquad (43)^*$$

The real-gas correction to this pseudo-perfect-gas enthalpy is therefore

$$\left(\frac{\bar{H}}{RT}\right)_{T,p,x_i} - \left(\frac{\bar{H}^o}{RT}\right)_{T,p,x_i} = \sum_i x_i \frac{H_i}{RT} - \sum_i x_i \frac{H_i^o}{RT} \tag{44}$$

or

$$\left(\frac{\bar{H} - \bar{H}^o}{RT}\right)_{T,p,x_i} = \sum_i x_i \left(\frac{H_i - H_i^o}{RT}\right)_{T,p} \tag{45}*$$

where the quantity $\left(\frac{H_i - H_i^o}{RT}\right)_{T,p}$ for each species is calculated from equation (30). The nondimensional enthalpy of the real-gas mixture at given values of T and p is found then by adding the resulting correction term from equation (45) to the pseudo-perfect-gas enthalpy given by equation (43).

In a similar manner the nondimensional real-gas entropy is determined. The pseudo-perfect-gas entropy of the mixture is

$$\left(\frac{\bar{S}^o}{R}\right)_{T,p,x_i} = \sum_i x_i \left(\frac{S_i^o}{R}\right)_{T,p} - \sum_i x_i \log_e x_i \tag{46}*$$

The real-gas correction to this pseudo-perfect-gas entropy is then

$$\left(\frac{\bar{S}}{R}\right)_{T,p,x_i} - \left(\frac{\bar{S}^o}{R}\right)_{T,p,x_i} = \sum_i x_i \left(\frac{S_i}{R}\right)_{T,p} - \sum_i x_i \left(\frac{S_i^o}{R}\right)_{T,p} \tag{47}$$

where the terms due to the entropy of mixing are canceled out, or finally

$$\left(\frac{\bar{S} - \bar{S}^o}{R}\right)_{T,p,x_i} = \sum_i x_i \left(\frac{S_i - S_i^o}{R}\right)_{T,p} \tag{48}*$$

The quantity $\left(\frac{S_i - S_i^o}{R}\right)_{T,p}$ for each species is calculated from equation (32). The nondimensional real-gas entropy of the mixture is found by adding the resulting correction term from equation (48) to the pseudo-perfect-gas entropy given by equation (46).

Summary of Calculation Procedure

The procedure used to calculate by means of the Lewis and Randall rule the real-gas composition and thermodynamic properties of a reacting gas mixture for a given temperature and pressure is presented in this section. First, the compressibility factor Z_i for each chemical species is calculated from equation (27). The values of x_i are obtained from simultaneous solution of equations (8), (9), and (19), with the appropriate values of $K_{\gamma,j}$ determined from equations (26) and (28). The nondimensional enthalpy and entropy correction terms for each pure species are then determined from equations (30) and (32), respectively. The value of $\overline{Z}$ for the mixture is found from equation (34), and the value of $\tilde{Z}$ is calculated from equations (36) and (38). The quantity Z' for the mixture is then calculated directly from equation (39). The specific volume of the mixture $\hat{v}$ can then be calculated from equation (37) or (39).

Where the objective of the foregoing calculation is to find the real-gas corrections to the thermodynamic properties of an equilibrium perfect-gas mixture which account for composition differences $x_i - x_i^o$ due to real-gas effects, the correction factors given by equations (41) and (42) are to be used. Then the real-gas nondimensional enthalpy and entropy are found by appropriate addition of these correction factors to the perfect-gas-mixture enthalpy $\overline{H}^o/RT$ and entropy $\overline{S}^o/R$.

COMMENTS ON THE APPLICABILITY OF THE LEWIS AND RANDALL RULE

In the next section a sample calculation using the present method is made for air, and the results are compared with the more rigorous calculations of Hilsenrath and Klein (ref. 4). The objective of the present section is to examine how well this sample calculation should compare with the results of reference 4 by establishing criteria for the applicability of the Lewis and Randall rule to arbitrary gas mixtures. This objective is accomplished by deducing the manner in which the Lewis and Randall rule accounts for unlike pair interactions.

The general virial equation of state for gas mixtures, ignoring virial coefficients greater than the second, is

$$\frac{pv}{RT} = 1 + \frac{1}{v}\sum_{i}\sum_{i'} x_i x_{i'} B_{ii'} = \overline{Z} \tag{49}$$

where $B_{ii'}$ is the second virial coefficient for the force interaction between species i and species i'. This equation of state was used in reference 4, and in the calculations made therein for air the $B_{ii'}$ coefficients were taken from Woolley's work (ref. 5). The equation of state resulting from the

application of the Lewis and Randall rule is $\frac{p\bar{v}}{RT} = \bar{Z}$ (eq. (34)) where $\bar{v} = \sum_i x_i v_i$. If it is required that equation (34) give the same compressibility factor as equation (49) for chosen values of T, p, and x_i, then the following condition must be satisfied:

$$\bar{v} = \sum_i x_i v_i$$

This condition becomes by solving for v from equation (49) and for v_i from equations (20) and (21) and by using $\sum_i x_i = 1$,

$$\sqrt{\left(1 + a \sum_i \sum_{i'} x_i x_{i'} B_{ii'}\right)} = \sum_i x_i \sqrt{1 + aB_i}$$

where $a \equiv \frac{4p}{RT}$ and $B_i \equiv B_{ii}$. Squaring this equation gives

$$\sum_i \sum_{i'} x_i x_{i'} \left(1 + aB_{ii'}\right) = \sum_i \sum_{i'} x_i x_{i'} \left[\sqrt{\left(1 + aB_i\right)}\right] \left[\sqrt{\left(1 + aB_{i'}\right)}\right]$$

Then a sufficient condition for the compressibility factors given by the Lewis and Randall rule and equation (49) to be equal is found by equating coefficients of the like $x_i x_{i'}$ terms and solving for $B_{ii'}$. The result is

$$B_{ii'} = \frac{\sqrt{\left(1 + aB_i\right)\left(1 + aB_{i'}\right)} - 1}{a} \qquad (50)$$

for all i - i' pair interactions. Equation (50) may also be interpreted as a prediction of the second virial coefficients for unlike pair interactions which are implied by the mixing procedure of the Lewis and Randall rule. These implied virial coefficients are pressure dependent but become functions only of temperature in the limits of zero and infinite pressure - that is, as $a \to 0$ and ∞, respectively. The limiting expressions of equation (50) are found to be

$$\lim_{a \to 0} B_{ii'} = \sqrt{B_i B_{i'}} \tag{51a}$$

and

$$\lim_{a \to \infty} B_{ii'} = \frac{B_i + B_{i'}}{2} \tag{51b}$$

These limits are recognized as two of the most frequently used empirical combination rules for computing second virial coefficients for unlike pairs from data on pure gases. Another semiempirical combination rule is the Lorentz expression

$$B_{ii'} = \frac{1}{8}\left(B_i^{1/3} + B_{i'}^{1/3}\right)^3$$

which always has a value between the limits given by equations (51a) and (51b). The Lorentz combination rule with modifications to account for nonspherical molecular shapes was used consistently in the work of reference 5. A discussion of these empirical combination rules may be found in references 1, 5, and 7.

Thus, for any mixture of gases the Lewis and Randall rule gives compressibility factors that are in good agreement with those found from equation (49) when the implied virial coefficients calculated by equation (50) are close to the accepted values for all important pair interactions. Because equation (50) is pressure dependent, there are only certain ranges of T and p which give good results for a particular mixture. In general, these T and p ranges are quite broad if the pure-gas virial coefficients for the preponderant species in the mixture are almost the same. This is the case, for example, for the calculation to be carried out for air at 6,000° K in the next section. However, for mixtures in which the pure-gas virial coefficients for the preponderant pair interactions are significantly different, the range of T and p for which the Lewis and Randall rule is applicable will be more limited. The applicability of the Lewis and Randall rule to reacting gas mixtures is also discussed in reference 2, and the analysis presented therein is consistent with the foregoing discussion.

Thus, the method presented in this paper for calculating real-gas corrections to the thermodynamic properties of reacting gas mixtures at high pressures is expected to give good results when (1) the only significant real-gas effect is accounted for by the second virial coefficient and (2) the virial coefficients predicted by equation (50) are in good agreement with the accepted coefficients for all preponderant pair interactions. The present method is not valid for gas mixtures in which ionization or chemical associations (not accounted for by chemical reactions) are important.

SAMPLE CALCULATION FOR AIR

Some results obtained for air by the present method of calculation are compared with the more rigorous results presented by Hilsenrath and Klein (ref. 4). The calculations presented in reference 4 consider the second virial coefficients for all pair interactions; virial coefficients higher than the second are ignored. These coefficients were obtained from reference 5 in which the virial coefficients for unlike pair interactions were estimated by certain empirical rules. The comparison is made at a temperature of 6,000° K and two relatively high pressures which correspond to conditions used in reference 4. The reason for this particular choice is that the chemical composition is tabulated in reference 4 along with the correction terms (difference between property based on a real gas and a perfect gas) for enthalpy and entropy at 6,000° K only. Two of the highest pressures presented in reference 4 were chosen for the comparison to make the real-gas effects as large as possible. The chemical composition at these conditions based on a perfect gas are also included.

The reference composition used for the present calculation was taken to be the same as that used in reference 4 - that is, 0.78084 mole fraction N_2, 0.20946 mole fraction O_2, 0.00934 mole fraction Ar, 0.00033 mole fraction CO_2, and 0.00003 mole fraction Ne. The following gaseous species were assumed to exist at the high-temperature state for the present calculation: NO_2, N_2O, CO_2, N_2, O_2, NO, CO, N, O, C, Ar, and Ne. The values of $K_{f,j}$ for each independent chemical reaction were taken to be the same as those used in reference 4. The required values of B_i and dB_i/dT for like pairs were obtained from reference 5.

Chemical-Composition Comparison

Table I presents the chemical composition of air obtained from the present method of calculation at 6,000° K and 2632.94 atm and 4415.30 atm; these pressures were chosen to equal two of the highest pressures for which the chemical composition of air was tabulated in reference 4. The chemical composition from reference 4 for these same conditions is included for comparison. The composition based on the assumption of a reacting mixture of perfect gases is also shown.

It is noted that the present calculation gives a chemical composition which agrees with that presented in reference 4 to 0.5 percent or less for each species considered with the exception of NO_2 and N_2O. The main reason that the mole fraction of NO_2 differs as much as it does from the value of reference 4 is that values of B_i and dB_i/dT for NO_2 were not available from reference 5. The quantity γ_{NO_2} in the mixture was, therefore, taken to be equal to unity. The mole fraction of N_2O calculated by the two methods differs by about 2 percent. This is believed to be a result of the basic difference between the two methods - that is, the manner in which the interactions between an N_2O molecule and any other gas particle are averaged.

It is seen also from a comparison of the real-gas and perfect-gas results in table I that the magnitude of the real-gas effect varies from one species to another and is, in general, rather small. As expected, the real-gas effect on the chemical composition increases with pressure. This comparison indicates that the present method of calculation adequately accounts for the real-gas effects in the determination of the chemical composition for these conditions.

Entropy and Enthalpy Comparisons

A direct comparison between the present calculation and the results of reference 4 for the enthalpy and entropy correction terms requires that a common basis be chosen. The correction terms (property differences) presented in reference 4 are based on a given temperature and specific volume and the real-gas composition. However, equation (45) for the enthalpy correction term for the present method is based on a given temperature and pressure rather than a given temperature and specific volume. Since the enthalpy of a perfect gas is a function of temperature only, it follows from equation (45) that

$$\left(\frac{\overline{H} - \overline{H}^{o}}{RT}\right)_{T,\overline{v},x_i} = \sum_i x_i \left(\frac{H_i - H_i^{o}}{RT}\right)_{T,p} \tag{52}$$

where p is the pressure of the real-gas mixture that corresponds to the state of the mixture at T, $\overline{v}$, and x_i. This equation was used to compare the results of the present calculation with correction terms presented in reference 4.

TABLE I.- CHEMICAL COMPOSITION OF AIR AT 6,000° K

Species	x_i^o	x_i (present calculation)	x_i (ref. 4)
		p = 2632.94 atm	
N_2	0.6602	0.6608	0.6608
O_2	.6690 × 10^{-1}	.7047 × 10^{-1}	.7023 × 10^{-1}
NO	.1560	.1554	.1551
NO_2	.9066 × 10^{-3}	[a].1136 × 10^{-2}	.1286 × 10^{-2}
N_2O	.1995 × 10^{-3}	.1817 × 10^{-3}	.1847 × 10^{-3}
O	.9987 × 10^{-1}	.9909 × 10^{-1}	.9942 × 10^{-1}
N	.3738 × 10^{-2}	.3675 × 10^{-2}	.3687 × 10^{-2}
CO	.2629 × 10^{-3}	.2619 × 10^{-3}	.2618 × 10^{-3}
CO_2	.5011 × 10^{-4}	.5128 × 10^{-4}	.5138 × 10^{-4}
C	.8927 × 10^{-8}	.8649 × 10^{-8}	.8648 × 10^{-8}
Ar	.8861 × 10^{-2}	.8865 × 10^{-2}	.8864 × 10^{-2}
Ne	.2846 × 10^{-4}	.2847 × 10^{-4}	.2847 × 10^{-4}
		p = 4415.30 atm	
N_2	0.6642	0.6653	0.6652
O_2	.7697 × 10^{-1}	.7780 × 10^{-1}	.7741 × 10^{-1}
NO	.1642	.1630	.1626
NO_2	.1297 × 10^{-2}	[a].1862 × 10^{-2}	.2252 × 10^{-2}
N_2O	.2727 × 10^{-3}	.2376 × 10^{-3}	.2423 × 10^{-3}
O	.8092 × 10^{-1}	.7967 × 10^{-1}	.8002 × 10^{-1}
N	.2895 × 10^{-2}	.2812 × 10^{-2}	.2825 × 10^{-2}
CO	.2513 × 10^{-3}	.2492 × 10^{-3}	.2490 × 10^{-3}
CO_2	.6508 × 10^{-4}	.6753 × 10^{-4}	.6771 × 10^{-4}
C	.6279 × 10^{-8}	.5946 × 10^{-8}	.5944 × 10^{-8}
Ar	.8954 × 10^{-2}	.8963 × 10^{-2}	.8963 × 10^{-2}
Ne	.2876 × 10^{-4}	.2879 × 10^{-4}	.2879 × 10^{-4}

[a]Values of B and dB/dT for NO_2 are not available from reference 5.

The nondimensional entropy correction term obtained from equation (48) applies only when the real-gas and perfect-gas calculations are based on the same temperature and pressure. Equation (48) can be modified by subtracting the quantity $\log_e \overline{Z}$ so that the correction term for the nondimensional entropy applies to a given temperature and specific volume. The modified equation is

$$\left(\frac{\overline{S} - \overline{S}^{o}}{R}\right)_{T,\overline{v},x_i} = \sum_i x_i \left(\frac{S_i - S_i^{o}}{R}\right)_{T,p} - \log_e \overline{Z} \tag{53}$$

The last term in equation (53) is equal to the change in $\overline{S}^{o}/R$ that would result from an isothermal change between the actual pressure of the mixture p and

the pressure that would be calculated from the perfect-gas equation of state based on the temperature T and specific volume $\overline{v}$ of the mixture. The composition of the mixture is held constant at its real-gas value for this calculation.

TABLE II.- ENTHALPY AND ENTROPY CORRECTIONS, COMPRESSIBILITY FACTORS, AND MOLECULAR WEIGHT RATIOS FOR AIR AT 6,000° K

	p = 2632.94 atm		p = 4415.30 atm	
	Present calculation	Reference 4	Present calculation	Reference 4
$\left(\frac{\overline{H} - \overline{H}^{\circ}}{RT}\right)_{T,\overline{v},x_i}$ . . .	0.1538	0.1615	0.2431	0.2524
$\frac{\overline{H}}{RT}$		5.4004		5.3823
$\left(\frac{\overline{S} - \overline{S}^{\circ}}{R}\right)_{T,\overline{v},x_i}$ . . .	-0.1213	-0.1270	-0.1917	-0.1986
$\frac{\overline{S}}{R}$		29.6019		28.9479
$\overline{Z}$	1.1375	1.1369	1.2172	1.2164
$\tilde{Z}$	1.0535	1.0537	1.0420	1.0420
Z'	1.1984	1.1979	1.2684	1.2675

Table II lists the enthalpy and entropy correction terms, the compressibility factors, and the molecular weight ratio for this sample approximate calculation for air and the corresponding results from reference 4. The real-gas quantities $\overline{H}/RT$ and $\overline{S}/R$ from reference 4 are included for comparison. It is seen that the real-gas effect on the enthalpy amounts to 3 percent at the lower pressure and about 5 percent at the higher pressure. The present calculation of the enthalpy correction term accounts for at least 95 percent of the correction obtained in the work of reference 4. A comparison of the correction terms for the entropy also shows good agreement between the present calculation and the results from reference 4.

Compressibility-Factor and Molecular-Weight-Ratio Comparisons

The total compressibility factor for the system Z' and the molecular weight ratio $\tilde{Z}$ for the present calculation are in excellent agreement with the values derived in reference 4. (See table II.) The real-gas effect on the equation of state is indicated by the quantity $\overline{Z}$. The calculated real-gas effect on the specific volume is 14 percent for the lower pressure and 22 percent for the higher pressure.

The good agreement between the present method and that of reference 4 for the calculations made is in part due to the fact that about two-thirds of the mixture is molecular nitrogen. Furthermore, the next preponderant species NO has a virial coefficient essentially equal to that of N_2 which also tends to improve the agreement.

CONCLUDING REMARKS

An approximate method based on the Lewis and Randall rule for calculating the chemical composition, compressibility factor, and the real-gas correction terms for enthalpy and entropy at high pressures has been developed. A comparison of results obtained from this method and the more rigorous calculations of Hilsenrath and Klein for air at 6,000° K and pressures of about 2,500 atm and 4,500 atm shows excellent agreement. The present method is simple to apply and should be expected to account for most of the real-gas effects in a number

of reacting gas mixtures at high pressures, provided the intermolecular force effects are adequately accounted for by the second virial coefficients of the mixture.

One advantage of the present approach is a reduction in machine computation time for the calculation of the equilibrium chemical composition because the individual equilibrium constants for the various reactions are not coupled to the composition of the reacting mixture. The more rigorous approach requires an iteration scheme between the chemical composition and the equilibrium constants for each reaction. For reacting systems in which the number of species is not too large, so that the solution of the chemical composition can be carried out as a hand calculation, the present method can be applied to include the real-gas effects by introducing only a few simple intermediate calculations.

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